

Site-Selective NMR in the Quasi-1D Conductor β - $\text{Sr}_{0.33}\text{V}_2\text{O}_5$

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Abstract

We report ^{51}V NMR experiments in the metallic phase of the quasi-one-dimensional (1D) conductor β - $\text{Sr}_{0.33}\text{V}_2\text{O}_5$. The Knight shift and the quadrupole splitting of all six vanadium sites were determined as a function of the direction of magnetic field perpendicular to the conducting b -axis. Magnetic properties of the three 1D structural units are remarkably heterogeneous. In particular, the V2 ladder unit shows pronounced charge disproportionation among the two (V2a and V2b) sites. At one of these sites, the absolute value of the Knight shift and $1/(T_1T)$ increase steeply with decreasing temperature, suggesting development of ferromagnetic correlation.

Key words: A. oxides, D. magnetic properties, D. nuclear magnetic resonance (NMR)

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1. Introduction

The family of quasi-one-dimensional mixed valent vanadium oxides β - $A_{0.33}\text{V}_2\text{O}_5$ ($A=\text{Li}, \text{Na}, \text{Ag}, \text{Ca}, \text{Sr},$ and Pb) exhibit a variety of exotic phenomena such as metal-insulator transition, charge ordering, and pressure-induced superconductivity [1,2]. They provide fascinating opportunities to study mechanism for competing orders in a common monoclinic crystal structure shown in Fig. 1 [3]. There are three types of one-dimensional V-O network extending along the most conducting b -axis: a zigzag chain formed by the V1 sites, another zigzag chain formed by the V3 sites, and a two-leg ladder formed by the V2 sites. At high temperatures, the A ions are distributed randomly over two sites with 50 % occupancy in the space group $C2/m$. They order below a certain temperature and fully occupy a single sites in the new space group $P2_1/a$. This doubles the unit cell along the b -axis and generates two inequivalent sites for each of the three vanadium sites, which are denoted as Vna and Vnb ($n=1-3$, see Fig. 1).

This ordering occurs above the room temperature (RM) in β - $\text{Sr}_{0.33}\text{V}_2\text{O}_5$, which is a Pauli paramagnetic metal at RT. It undergoes a metal-insulator transition at $T_{\text{MIT}} \sim 170$ K accompanied by a simultaneous structural transition, that further triples the unit cell along the b -axis [3,4]. The magnetic susceptibility in the low T insulating phase indi-

cates a singlet ground state with a spin gap. A spatial order of vanadium valence into V^{4+} ($3d^1$) and V^{5+} ($3d^0$) with

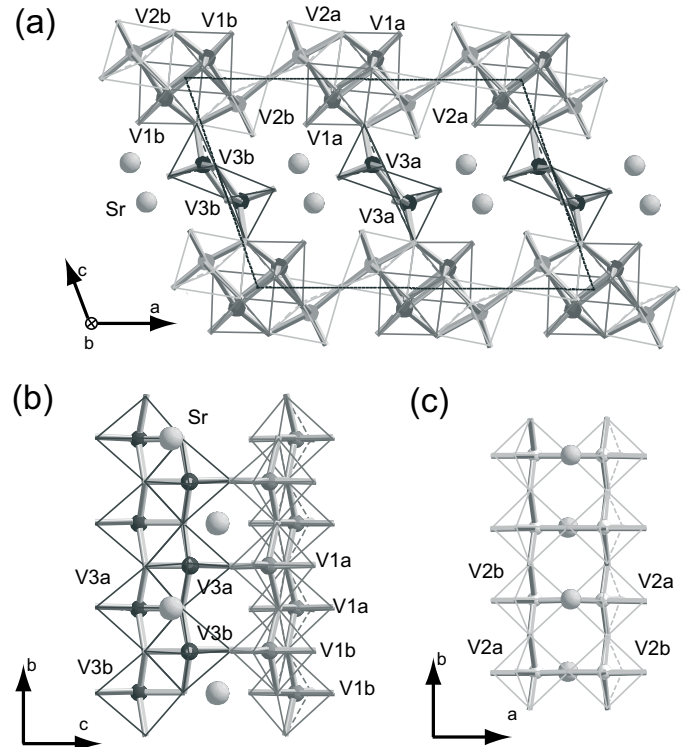


Fig. 1. Crystal structure of β - $\text{Sr}_{0.33}\text{V}_2\text{O}_5$ with the space group $P2_1/a$ viewed from the (a) b -, (b) a^* -, and (c) c -directions.

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1:2 ratio was suggested for the low T phase from structural analysis. However, the neutron diffraction [5] and the nuclear magnetic resonance (NMR) [6] experiments ruled out such atomic localization of d electrons for β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$, which also shows simultaneous metal-insulator and structural transitions. In this paper we report results of ^{51}V -NMR experiments on a single crystal of β - $\text{Sr}_{0.33}\text{V}_2\text{O}_5$ and discuss charge distribution and spin dynamics in the high T metallic phase. NMR data on β - $\text{Sr}_{0.33}\text{V}_2\text{O}_5$ have been reported only for a powder sample so far [7].

2. Experiment

A single crystal of β - $\text{Sr}_{0.33}\text{V}_2\text{O}_5$ obtained by the Czochralski method was used in this work. It has the size $0.5 \times 1.8 \times 0.2 \text{ mm}^3$ with the largest dimension along the b -axis. The ^{51}V NMR spectra were obtained by summing the Fourier transform of the spin-echo signals with the frequency step of 0.3 MHz. The nuclear spin-lattice relaxation rate $1/T_1$ was measured by the inversion recovery method. The magnetic field H_0 (10.509 T) was applied in the ac -plane. The direction of the field is specified by the angle (θ) measured from the a -axis.

3. Results and Discussions

There are four V atoms for each of the six crystallographic sites in a unit cell of the metallic phase (space group $P2_1/a$). When the magnetic field is applied in the ac -plane, these four atoms become equivalent and give identical NMR spectra. Since ^{51}V nuclei have spin $I=7/2$, the electric field gradient (EFG) splits the NMR spectrum into equally spaced seven lines at the following frequencies due to first order effect of the nuclear quadrupole interaction,

$$\nu_m(\theta) = \{1 + K(\theta)\}\gamma H_0 + (m - 1/2)\nu_Q(\theta), \quad (1)$$

where γ is the nuclear gyromagnetic ratio (11.193 MHz/T), $K(\theta)$ is the Knight shift, $\nu_Q(\theta)$ is the quadrupole splitting, and m specifies the nuclear transitions $I_z = m \leftrightarrow m - 1$.

The upper panel of Fig. 2 shows the NMR spectrum at $\theta = -1^\circ$, while the lower panel displays the angle dependence of the resonance frequencies for all the lines at $T=190 \text{ K}$. At each angle, there are several sets of equally spaced lines assigned as A - F. In many cases only a portion of the quadrupole split seven lines are clearly resolved. However, they are sufficient to determine $K(\theta)$ and $\nu_Q(\theta)$ from Eq. (1). In Fig. 3(a) and (b), we plot the angle dependences of $K(\theta)$ and $\nu_Q(\theta)$ for the A - F sites. Since $K(\theta) \ll 1$ and $\nu_Q(\theta) \ll \gamma H_0$, we need consider only the lowest order effect for the frequency shift. Then $K(\theta)$ and $\nu_Q(\theta)$ should obey the following angle dependences [9],

$$\begin{aligned} K(\theta) &= K_1 + K_2 \cos^2(\theta - \psi_K) \\ \nu_Q(\theta) &= \nu_1 + \nu_2 \cos^2(\theta - \psi_Q). \end{aligned} \quad (2)$$

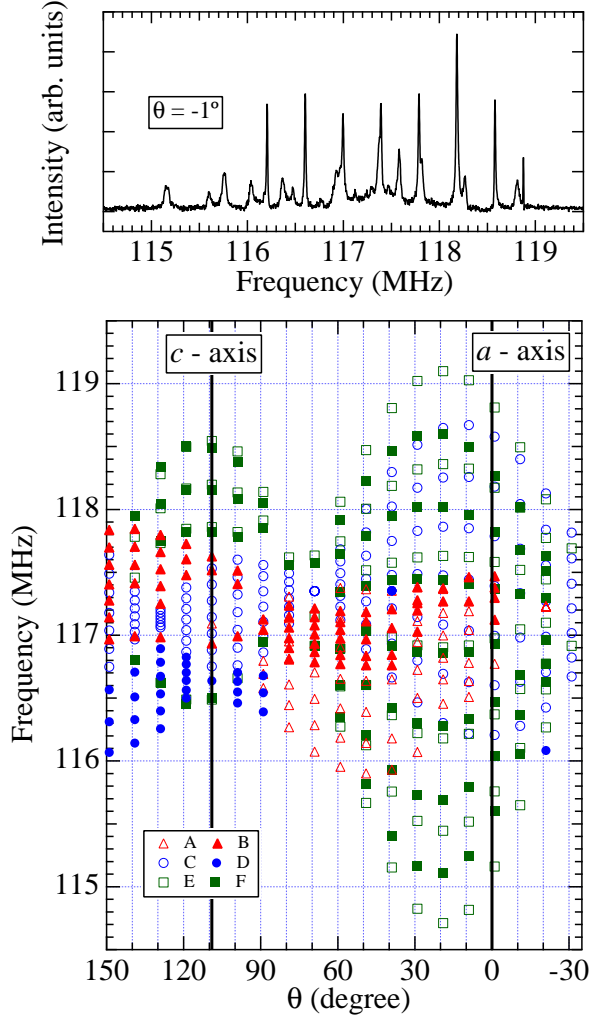


Fig. 2. An example of the NMR spectrum at (upper panel) and the angle dependence of the NMR frequency of all the observed lines (lower panel) at $T=190 \text{ K}$.

These equations indeed fit the data very well as shown by the solid, dashed and dotted lines in Fig. 3(a) and (b). Thus we have completely determined $K(\theta)$ and $\nu_Q(\theta)$ for all the vanadium sites.

Generally the Knight shift at transition metal sites consists of the orbital and the spin contributions, $K(\theta) = K_{\text{orb}}(\theta) + K_{\text{spin}}(\theta)$. While K_{spin} may be either negative or positive, K_{orb} is always positive. The fact that $K(\theta)$ is negative for the entire range of angle at all sites indicates that the dominant term is K_{spin} , which is related to the local spin susceptibility as $K_{\text{spin}}(\theta) = \{A_{\text{cp}} + A_{\text{dip}}(\theta)\}\chi_{\text{spin}}$. The core polarization coupling constant A_{cp} is isotropic and negative, while the dipolar coupling constant $A_{\text{dip}}(\theta)$ is purely anisotropic, i.e. its directional average is zero. Since χ_{spin} is nearly isotropic except for small anisotropy of the g -value, the observed angular variation of $K(\theta)$ must be ascribed to the anisotropy of $A_{\text{dip}}(\theta)$, which is determined by the spin density distribution of d -electrons.

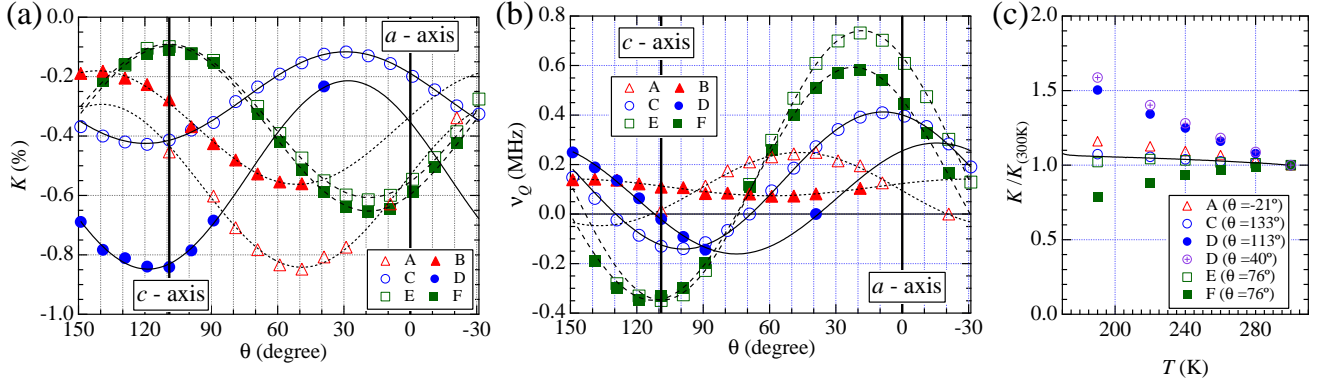


Fig. 3. Angle dependence of (a) K and (b) ν_Q for all sites at $T=190$ K. The solid lines show the fitting to Eq. (2). (c) T -dependences of K normalized by the value at 300 K (symbols) and the bulk susceptibility (the solid line).

In β - $\text{Sr}_{0.33}\text{V}_2\text{O}_5$, each vanadium atom is surrounded by a distorted squared pyramid formed by oxygen atoms. The shortest vanadyl bonding between the vanadium and the apical oxygen lies nearly in the ac -plane for all the V sites (within 4°). Doublet and Lepetit investigated the local electronic structure based on the extended Hückel tight-binding calculation [8]. They proposed that the magnetic orbital accommodating the d -electrons is the d_{xy} -orbital, where the local z -axis is parallel to the shortest V-O bonding and x and y point toward the oxygen atoms in the basal plane of the pyramid. The dipolar coupling A_{dip} to the spin density on the d_{xy} -orbital takes the largest negative value when the field is along the z -axis. Since A_{cp} is negative, $K(\theta)$ is expected to be most negative when the field is along the shortest V-O bond direction.

In table 1 we compare the values of ψ_K at which $K(\theta)$ becomes most negative (upper panel) with the directions of the shortest V-O bonding projected onto the ac -plane obtained from the structural data in Ref. [3] (lower part). We can immediately assign the three groups of sites (A, B), (C, D) and (E, F) to the (V1a, V1b), (V2a, V2b) and (V3a, V3b) sites, respectively. We cannot determine, however, which one in each group corresponds to "a" or "b". With this assignment the directions for the minimum of $K(\theta)$ and the shortest V-O bonding agree within ten degrees, supporting that the magnetic orbital indeed has d_{xy} symmetry.

The data in Fig. 3(a) indicate that while $K(\theta)$ for the V3a and V3b sites are almost identical, it differs substantially between the V2a and V2b sites and between the V1a and the V1b sites. In particular, the amplitudes of the angular

variation of $K(\theta)$ (K_2 in Eq. 2) for the V2a and the V2b sites differ by a factor two. Since the angular variation of $A_{\text{dip}}(\theta)$ should be similar for all the sites, the local spin susceptibility χ_{spin} must be significantly different for the V2a and the V2b sites. Such alternation of χ_{spin} should be ascribed to charge disproportionation. In other words, although the d -electron density is quite uniform in the V3 zigzag-chains, it alternates strongly in the V2 ladders. The strong charge disproportionation even in the metallic phase may appear surprising. However, this has been predicted by Doublet and Lepetit. They argued that ordering of Sr leads to a large difference in the energy of the d -levels, therefore, the different charge density at the V2a and the V2b sites [8]. On the other hand, the three groups of sites, V1, V2, and V3, show quite similar values of K_2 when averaged over the "a" and the "b" sites. Thus the d -electrons are distributed rather uniformly over the three 1D structural units.

The V2a and the V2b sites exhibit also distinct T -dependence of the Knight shift. Figure 3(c) show the T -dependence of K for several sites normalized by the value at $T=300$ K. They were measured at "magic angles" at which $\nu_Q(\theta)=0$. (No measurements were done for the B sites which do not have a magic angle in the ab -plane.) The steep increase of $|K|$ at the D sites with decreasing temperature is in strong contrast to the nearly constant behavior at the C sites. We also note peculiar decrease of $|K|$ with decreasing temperature at the F sites. Although the bulk susceptibility shows little T -dependence (the solid line), this must be a results of cancellation of opposite T -dependence at the D and F sites. We should mention that such strong heterogeneity within the same structural unit has not been observed in β - $\text{Na}_{0.33}\text{V}_2\text{O}_5$ [10]

The angle dependence of $\nu_Q(\theta)$ shown in Fig. 3(b) also reflects the local symmetry of each V sites. There is indeed noticeable correlation between the directions of shortest V-O bonding and extrema of $\nu_Q(\theta)$ for many sites. However, EFG is rather difficult to analyze because of contributions not only from the on-site d -electrons but from the neighboring ions. Hence we did not attempt to make any quantitative analysis.

Table 1

The upper part lists the values of ψ_K for the A to F sites. The lower part shows the directions of the shortest V-O vanadyl bonding projected onto ac plane. The angles were measured from the a -axis.

Sites	A	B	C	D	E	F
ψ_K	49.5°	51.3°	120.1°	119.2°	19.7°	19.7°
Sites	V1a	V1b	V2a	V2b	V3a	V3b
V-O bond	43°	45°	110°	117°	22°	22°

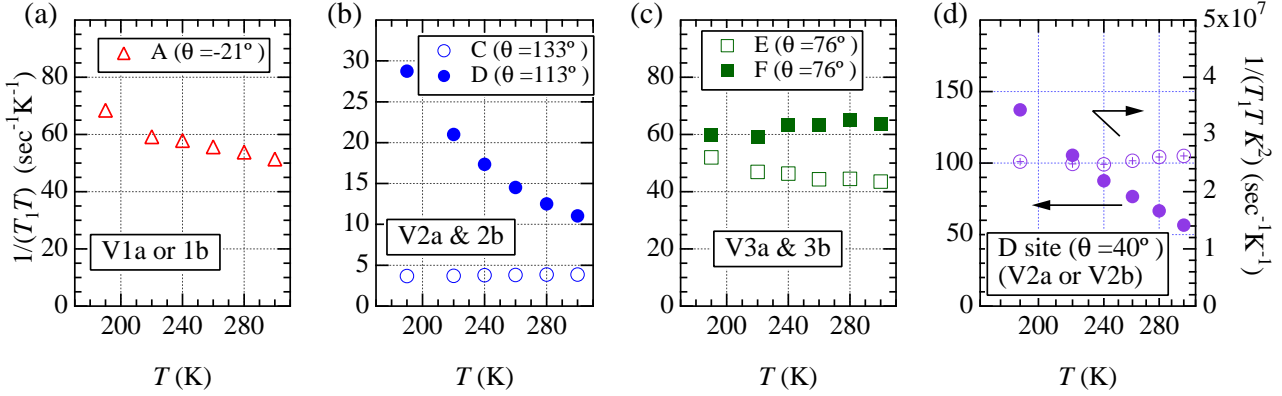


Fig. 4. T dependence of $1/T_1T$ at various sites measured with the field along the magic angle indicated in each panel. Also shown in (d) is $1/(T_1TK^2)$ at the D sites.

We now discuss the spin dynamics. The nuclear relaxation rate $1/T_1$ was measured also with the field along magic angles. This enabled site-selective measurements of $1/T_1$ even when the line is not well isolated from others, due to strongly enhanced signal, distinct rf-pulse width for optimum excitation, and simple exponential time dependence of the nuclear magnetization recovery at magic angles. For the E and F sites, which have nearly the same magic angle, the nuclear recovery curve was fit to sum of two exponential functions. The result was checked by separate experiments on well isolated quadrupole satellite lines.

The T -dependences of $1/(T_1T)$ are shown in Fig. 4. Again different sites show remarkably contrasting behavior. The V3a and V3b sites (E and F) show nearly constant behavior with the similar magnitude of $1/(T_1T)$, suggesting absence of strong spin correlations. Precisely speaking, however, the E sites show slight increase of $1/(T_1T)$ with decreasing temperature. Such increase is more clearly visible for the A sites (one of the V1 sites). The results for the V2a and V2b (C and D) sites are most anomalous. While $1/(T_1T)$ at the C sites is nearly constant, it increases strongly at the D sites with decreasing temperature. At the D sites, $1/(T_1T)$ and K^2 follow approximately the same T -dependence as indicated by nearly constant $1/(T_1TK^2)$ shown in Fig. 4(d).

Generally for quasi 1D electron systems, spin fluctuations both at $q \sim 0$ and at $q \sim 2k_F$ contribute to $1/(T_1T)$,

$$1/(T_1T) = 1/(T_1T)_{q \sim 0} + 1/(T_1T)_{q \sim 2k_F}. \quad (3)$$

In the Luttinger-liquid (LL) theories, which is expected to be applicable to quasi 1D conductors, the T -dependence of each term is given as $1/(T_1T)_{q \sim 0} \propto \chi_{spin}^2$, $1/(T_1T)_{q \sim 2k_F} \propto T^{K_\rho-1}$, where $K_\rho=1$ for non-interacting electrons but generally $0 < K_\rho < 1$ for repulsive interactions [11,12]. The nearly constant behavior of $1/(T_1TK^2)$ (Fig. 4(d)) suggests that the dominant contribution to $1/(T_1T)$ at the D sites comes from $q \sim 0$ spin fluctuations. Thus our results appear to support strong ferromagnetic correlation in the V2 ladder units in the high T metallic phase. Another peculiar result is the nearly constant behavior of $1/(T_1T)$ at the F sites, in spite of the substantial decrease of the Knight shift

with decreasing temperature.

4. Conclusion

We performed site-selective ^{51}V NMR measurements on a single crystal of $\beta\text{-Sr}_{0.33}\text{V}_2\text{O}_5$ in the high T metallic phase. We found that the magnetic properties are remarkably heterogeneous even within the same structural unit. In particular, the V2 ladder unit shows strong charge disproportionation caused by the Sr ordering. At one of the V2 sites, the absolute value of the Knight shift and $1/(T_1T)$ increases strongly with decreasing temperature, indicating development of ferromagnetic correlation. The local spin susceptibility at one of the V3 sites decreases substantially with decreasing temperature, although $1/(T_1T)$ is nearly constant.

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